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(54) LITHIUM MANGANESE-BASED OXIDE, HAVING SPINEL STRUCTURE AND  
 CONTAINING ANOTHER KIND OF ELEMENT, ITS PRODUCTION AND USE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress the elution of Mn in an organic electrolytic solution of a lithium secondary battery by using a lithium manganese-based oxide having a spinel structure of a specific chemical composition containing at least another kind of element other than Li and Mn as a material of a positive electrode.

$$[Li]_x [Li_{1-x}M_yMn_{2-4-y}]O_{4+x}$$

SOLUTION: This lithium manganese-based oxide having a spinel structure is represented by the formula [the interior of { } denotes the position of an oxygen tetrahedron in the structure; the interior of [ ] denotes the position of an oxygen octahedron in the structure;  $0 < (x) \leq 0.33$ ;  $0 < (y) \leq 1$ ;  $-0.5 < (d) < 0.8$ ] and contains at least

another element (M) other than Li and Mn. The crystal structure is a cubic crystal and the lattice constant (a) is  $\geq 8.19$  and  $\leq 8.24$  Å. The other element M is selected from Be, Mg, Ca, Y, Ti, V, Cr, Fe, Cu, B, Al, Si, Pb, P and the like. Furthermore, the oxide preferably has 1-50  $\mu\text{m}$  average agglomerated particle diameter, 0.1-5  $\text{m}^2/\text{g}$  BET specific surface area and  $\leq 3$   $\mu\text{m}$  average primary particle diameter. The lithium manganese-based oxide containing the other element is produced by mixing respective compounds of the Mn, Li and the other element and baking the resultant mixture.

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CLAIMS

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[Claim(s)]

[Claim 1] A Spinel structure lithium manganese system oxide which is expressed with the following presentations and contains at least one kind of other type elements other than Li and Mn (M).

{Li} [Lix-My-Mn(2-x-y)] O<sub>4+d</sub> (however, {} -- inside -- an oxygen tetrahedral site in structure, and [] -- inside expresses an oxygen octahedral site in structure.)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ , and M are elements other than Li and Mn.

[Claim 2] A Spinel structure lithium manganese system oxide containing an other type element according to claim 1 whose crystal structure is a cubic and the lattice constant a of whose is 8.19Å or more and 8.24Å or less.

[Claim 3] These M elements That they are at least one sort of elements chosen from a group of Be, Mg, calcium, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Fe, Co, nickel, Cu, Ag, Zn, B, aluminum, Ga, In, Si, germanium, Sn, Pb, P, As, Sb, and Bi A Spinel structure lithium manganese system oxide containing an other type element of claim 1 and 2 publications by which it is characterized.

[Claim 4] A Spinel structure lithium manganese system oxide containing an other type element according to claim 1 to 3 characterized by for a diameter of average floc being 1-50 micrometers, and a BET specific surface area being 0.1-5m<sup>2</sup>/g.

[Claim 5] A Spinel structure lithium manganese system oxide containing an other type element according to claim 1 to 4 characterized by the first [ an average of ] particle diameter being 3 micrometers or less.

[Claim 6] A Spinel structure lithium manganese system oxide containing an other type element according to claim 1 to 5 characterized by M being Cr.

[Claim 7] A Spinel structure lithium manganese system oxide containing an other type element characterized by being  $0 < x \leq 0.15$  and  $0.02 \leq y \leq 0.2$  in claim 6.

[Claim 8] A Spinel structure lithium manganese system oxide containing an other type element which other type elements M other than Li and Mn are two kinds of elements (M (1), M (2)), and is expressed with the following formula in a Spinel structure lithium manganese system oxide containing an other type element according to claim 1 to 5.

Lix-Mn<sub>2-x-y1-y2</sub>, M(1) y<sub>1</sub>, and {Li} [M(2) y<sub>2</sub>] O<sub>4+d</sub> (however, {} -- inside -- an oxygen tetrahedral site in structure, and [] -- inside expresses an oxygen octahedral site in structure.)  $0 < x \leq 0.33$ ,  $0 < y_1 + y_2 \leq 1.0$ ,  $-0.5 < d < 0.8$

[Claim 9] A Spinel structure lithium manganese system oxide containing an other type element according to claim 8 characterized by one sort [ of an other type element to contain ] M (1) being Cr.

[Claim 10] A Spinel structure lithium manganese system oxide with which M (1) is Cr among other type elements to contain, and M (2) contains claim 8 characterized by being a metal, and an other type element of nine publications at least in \*\*.

[Claim 11] A Spinel structure lithium manganese system oxide containing an other type element according to claim 8 to 10 characterized by for M (1) being Cr among other type elements to contain, and M (2) being Fe.

[Claim 12] A Spinel structure lithium manganese system oxide containing an other type element according to claim 11 characterized by being  $0 < x \leq 0.15$ ,  $0 < y_1 \leq 0.2$ , and  $0 < y_2 \leq 0.2$ .

[Claim 13] A manufacture method of a Spinel structure lithium manganese system oxide containing an other type element according to claim 1 to 12 characterized by using a manganic acid ghost whose diameter of average floc is 0.5-50 micrometers as a raw material manganese compound in a method of manufacturing a Spinel structure lithium manganese system oxide which contains an other type element by mixing and calcinating a manganese compound, a lithium compound, and a compound of a content other type element.

[Claim 14] A manufacture method of a Spinel structure lithium manganese system oxide containing an other type element characterized by shaping density of a raw material manganese compound according to claim 13 being three or more 2.7 g/cm.

[Claim 15] A manufacture method of a Spinel structure lithium manganese system oxide which contains Na contained in a raw material manganese compound, and an other type element characterized by the amount of K being 500 ppm or less in a manufacture method of a Spinel structure lithium manganese system oxide containing claim 13 and an other type element given in 14.

[Claim 16] A manufacture method of a Spinel structure lithium manganese system oxide which contains an other type element characterized by a BET specific surface area of a raw material lithium compound being more than 1m<sup>2</sup>/g in a manufacture method of a Spinel structure lithium manganese system oxide containing an other type element according to claim 13 to 15.

[Claim 17] A manufacture method of a Spinel structure lithium manganese system oxide containing an other type element characterized by using a lithium carbonate as a raw material lithium compound in a manufacture method of a Spinel structure lithium manganese system oxide containing an other type element according to claim 16.

[Claim 18] A manufacture method of a Spinel structure lithium manganese system oxide containing an other type element characterized by for burning temperature being 500-1000 degrees C, and a firing environments being among atmospheric air in a manufacture method of a Spinel structure lithium manganese system oxide containing an other type element according to claim 13 to 17.

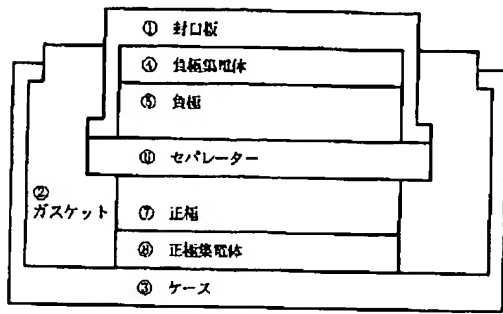
[Claim 19] A manufacture method of a Spinel structure lithium manganese system oxide which contains an other type element characterized by calcinating after corning in a manufacture method of a Spinel structure lithium manganese system oxide containing an other type element according to claim 13 to 18 after mixing a manganese compound, a lithium compound, and a compound of a content other type element.

[Claim 20] Li rechargeable battery characterized by using a content Spinel structure lithium manganese system oxide for an other type element according to claim 1 to 12 as positive active material in Li rechargeable battery which consists of nonaqueous electrolyte and a separator which dissolved a positive electrode, a negative electrode, and an electrolyte containing Li.

[Claim 21] Li rechargeable battery characterized by setting to Li rechargeable battery of claim 20, and using as a negative-electrode active material a carbon system material electrochemically inserted and desorbed from a lithium ion.

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[Translation done.]

Drawing selection drawing 1

[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the Spinel structure lithium manganese system oxide containing other type elements other than Li and Mn (M), and its manufacture method list use.

[0002] A manganic acid ghost is a material used for many years as a cell active material. The lithium manganic acid ghost which is the quality of a composite of manganese and a lithium, and the lithium manganese system oxide which replaced some manganese of this lithium manganic acid ghost by the other type element are materials which attract attention in recent years as positive active material of the lithium secondary battery which can attain high power and high energy density.

[0003]

[Description of the Prior Art] It is called for that the positive-electrode material for lithium secondary batteries has high that a voltage operating space is high, that it is high discharge capacity, and cycle stability, and the multiple oxide of \*\*s, such as Li and various metals, for example, Co, nickel, Mn, etc., is examined.

[0004] If it is known that the two-step discharge with a flat part portion is shown and the 4V neighborhood and the 3V neighborhood can be made to carry out the cycle of  $\text{LiMn}_2\text{O}_4$  of the Spinel structure which is a kind of the multiple oxide of Li and Mn reversibly in the operating space of the 4V neighborhood at the time of discharge, since it can expect to take out high energy, it is thought that it is promising as positive active material.

[0005] However, when Mn in  $\text{LiMn}_2\text{O}_4$  structure performed charge and discharge as a lithium secondary battery positive electrode, it turned out that it is eluted in organic electrolysis liquid in recent years. Furthermore, in the experiment of this invention persons, it was based on the class of electrolytic-solution system, and even if it did not perform charge and discharge, having saved  $\text{LiMn}_2\text{O}_4$  at 85 degrees C in organic electrolysis liquid also turned out that the amount of Mn in structure was eluted also about 1mol%, and the property as a positive-electrode material fell remarkably after elution.

[0006] It only saved for a long period of time, Mn in structure is eluted in organic electrolysis liquid, and this shows a possibility of stopping operating as a positive electrode for lithium secondary batteries, even if it does not perform charge and discharge, when  $\text{LiMn}_2\text{O}_4$  is used as a positive electrode for lithium secondary batteries.

[0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the highly efficient lithium secondary battery which used for the positive electrode the highly efficient Spinel structure lithium manganese system oxide and this lithium manganese system oxide which controlled Mn elution in the inside of organic electrolysis liquid as a positive-electrode material for Li rechargeable batteries.

[0008]

[Means for Solving the Problem] As a result of this invention persons' inquiring wholeheartedly, it was expressed with the following presentations and a Spinel structure lithium manganese system oxide containing variety elements other than Li and Mn found out that the above-mentioned purpose could be attained.

[0009]

{Li} [Lix-My-Mn(2-x-y)] O<sub>4+d</sub> (however, { } -- inside -- an oxygen tetrahedral site in structure (8a site), and [ ] -- inside expresses an oxygen octahedral site in structure (16d site).)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ .

[0010] If a firing environments is a reducing atmosphere, this d value will turn into a value of minus, and will turn into a value of plus in an oxidizing atmosphere. M is elements other than Li and Mn.

[0011] Furthermore, a highly efficient lithium secondary battery using a Spinel structure lithium manganese system oxide containing a manufacture method of a Spinel structure lithium manganese system oxide containing Li of this invention and other type elements other than Mn (M), Li of this invention, and other type elements other than Mn (M) as positive active material was found out, and this invention was completed.

[0012]

[Function] Hereafter, this invention is explained concretely.

[0013] The Spinel structure lithium manganese system oxides containing Li of this invention and other type elements other than Mn (M) are the following presentations.

[0014]

{Li} [Lix-My-Mn(2-x-y)] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [ ] -- inside expresses the oxygen octahedral site in structure.)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$ , and M are elements other than Li and Mn.

It exists in the oxygen tetrahedral site in structure, the crystal structure is cubic Spinel structure as a product, and, as for these M elements, what forms the Spinel structure lithium manganese system oxide the lattice constant a of whose is 8.19Å or more and 8.24Å or less is desirable.

[0015] In addition, as Spinel structure other than a cubic, although there is \*\*\*\*\* etc., it becomes [ the energy taken out when action potential becomes low and constitutes Li rechargeable battery ] small and is not desirable.

[0016] moreover, the lattice constant a -- the above -- if it becomes out of range, since the manganese in the structure will become unstable, Mn elution volume becomes large and is not desirable.

[0017] These M elements are at least one sort of elements chosen from the group of Be, Mg, calcium, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Fe, Co, nickel, Cu, Ag, Zn, B, aluminum, Ga, In, Si, germanium, Sn, Pb, P, As, Sb, and Bi.

[0018] It is desirable that the diameter of average floc of the Spinel structure lithium manganese system oxide which furthermore contains the other type element of this invention is 1-50 micrometers, and a BET specific surface area is 0.1-5m<sup>2</sup>/g.

[0019] When the diameter of average floc is larger than this range, or when a BET specific surface area is smaller than this range An elevated temperature is required for manufacture, and since the high engine performance is hard to be obtained when it is used for a cell active material, are not desirable. Conversely, when the diameter of average floc is smaller than this range, or when a BET specific surface area is larger than this range, when using it for a cell active material, restoration nature is bad, and the problem of Mn tending to be eluted out of structure is easy to be generated and is not desirable.

[0020] Moreover, as for the first [ an average of ] particle diameter of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is desirable that it is 3 micrometers or less. When larger than this range, since the high engine

performance is hard to be obtained when it is used for a cell active material etc., it is not desirable.

[0021] y showing the amount of the other type element of the Spinel structure lithium manganese system oxide containing the other type element of this invention is the content of each other type element, when it is  $0 < y \leq 1.0$  and contains two or more sorts of other type elements  $y_1$ ,  $y_2$ , and  $y_3$  ... It is referred to as  $y_n$  and is  $0 < y_1 + y_2 + y_3 + \dots$  It is  $+y_n \leq 1.0$ .

[0022] this -- charge-and-discharge capacity of the total amount of y decreases, and it is not desirable at 1.0 or more. The amount x which exists in the oxygen octahedral site at the time of setting to 1 the amount which Li in the Spinel structure lithium manganese system oxide containing the other type element of this invention exists in both the oxygen tetrahedral site in structure and an oxygen octahedral site, and exists in an oxygen tetrahedral site is  $0 < x \leq 0.33$ .

[0023] It becomes [ the single phase structure of Spinel structure is not acquired, or the elution volume of Mn to the inside of organic electrolysis liquid becomes large, and / also when larger than this range / charge-and-discharge capacity ] small preferably, and is not desirable when the total amount of Li is less than one.

[0024] this -- in the case of  $0 \leq x \leq 0.15$ , a large capacity can be taken, and Mn elution volume is stopped low, and the value of x is especially desirable.

[0025] Cr is desirable when the number of elements other than Li of this invention and Mn is one.

[0026] When an other type element is Cr, the empirical formula is as follows.

[0027]

{Li} [Lix-Mn<sub>2-x-y</sub>-Cry] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [ ] -- inside expresses the oxygen octahedral site in structure.)  $0 < x \leq 0.33$ ,  $0 < y \leq 1.0$ ,  $-0.5 < d < 0.8$

In this case, it is desirable that it is  $0 < x \leq 0.15$  and  $0.02 \leq y \leq 0.2$ . Furthermore, other type elements other than Li and Mn are expressed with the following formula when it contains two sorts (M (1), M (2)).

[0028] Lix-Mn<sub>2-x-y1-y2</sub>, M(1) y<sub>1</sub>, and {Li} [M(2) y<sub>2</sub>] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [ ] -- inside expresses the oxygen octahedral site in structure.)  $0 < x \leq 0.33$ ,  $0 < y_1 + y_2 \leq 1.0$ ,  $-0.5 < d < 0.8$ , M (1), and M (2) are elements other than Li and Mn. It is desirable that one sort [ of the other type element to contain ] M (1) is Cr, and, as for M (2), it is desirable that at least \*\* is a metal.

[0029] It is more desirable that M (1) is Cr among the other type elements to contain, and M (2) is especially Fe, and it is expressed with the following formula in that case.

[0030] {Li} [Lix-Cry<sub>1</sub>, Fey<sub>2</sub>, and Mn<sub>2-x-y1-y2</sub>] O<sub>4+d</sub> (however, { } -- inside -- the oxygen tetrahedral site in structure, and [ ] -- inside expresses the oxygen octahedral site in structure.)  $0 < x \leq 0.33$ ,  $0 < y_1 \leq 0.5$ ,  $0 < y_2 \leq 0.5$ ,  $-0.5 < d < 0.8$

In this empirical formula, it is desirable that it is  $0 < x \leq 0.15$ ,  $0 < y_1 \leq 0.2$ , and  $0 < y_2 \leq 0.2$ .

[0031] When content Spinel structure lithium manganese system oxides are Li, Mn, and a Spinel structure lithium manganese system oxide that contains at least one kind of other type elements other than Li and Mn (M) further and use Li for a cell active material or Li adsorption material for the other type element of this invention further as mentioned above in the oxygen tetrahedral site in structure at an oxygen octahedral site, it has the particulate structure which becomes highly efficient.

[0032] A content Spinel structure lithium manganese system oxide can carry out the manufacture method of the other type element of above-mentioned this invention by mixing a manganese compound, a lithium compound, and the compound of a content other type element, and calcinating.

[0033] Be [ what is necessary / just although the compound to mix can generate an oxide



below with burning temperature in an oxide a hydroxide, an oxidation hydroxide, a carbonate, a chloride salt, a nitrate, a sulfate, etc. ], especially an oxide, a hydroxide, an oxidation hydroxide, and a carbonate are desirable from the effect which it has to the environment of reactivity and waste gas.

[0034] It is indispensable to use the manganic acid ghost whose diameter of average floc is 0.5-50 micrometers as a raw material manganese compound, and it is desirable to use that whose shaping density of the raw material manganese compound is three or more 2.7 g/cm.

[0035] Since it is difficult to obtain what satisfies the fine-particles property of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is not desirable to use the manganic acid ghost outside this range.

[0036] It is desirable to use Na furthermore contained in a raw material manganese compound and the thing whose amount of K is 500 ppm or less, and when there were many these Na and amounts of K and a product is used for a cell active material, it is difficult to create highly efficient Li rechargeable battery.

[0037] In the manufacture method of the Spinel structure lithium manganese system oxide containing the other type element of this invention, it is desirable to use the lithium compound whose BET specific surface area is more than 1m<sup>2</sup>/g as a raw material lithium compound.

[0038] If a carbonate, a nitrate, a chloride salt, a hydroxide, an oxide, etc. are illustrated as a lithium compound and the lithium carbonate especially whose BET specific surface area is more than 1m<sup>2</sup>/g is used, also in atmospheric air, the Spinel structure lithium manganese system oxide which contains a uniform other type element easily can be manufactured, and it is very desirable.

[0039] Burning temperature [ in / for the other type element of this invention / manufacture of a content Spinel structure lithium manganese system oxide ] is suitably chosen so that a desired fine-particles property may be acquired from the range of 500-1000 degrees C.

[0040] burning temperature – this – it is hard to become the range of the request of the BET specific surface area and/or the diameter of a primary particle of a product by being out of range and is not desirable.

[0041] Although both the inside of atmospheric air and the oxygen rich ambient atmosphere of the ambient atmosphere at the time of baking are usable, the ease of the structure of a firing furnace to the inside of atmospheric air is desirable.

[0042] In the aforementioned manufacture conditions, especially the thing for which the method shown below is adopted is desirable.

[0043] 1. How to calcinate, after mixing manganese compound, lithium compound, and compound of other type element and corning.

[0044] 2. How to calcinate, after calcinating, mixing lithium compound and/or compound of content other type element and corning [ mixing, a granulation, and ] manganese compound and lithium compound.

[0045] 3. Calcinate after mixing any one sort of a manganese compound, a lithium compound, and the compound of a content other type element after calcinating, mixing, a granulation, and, and corning a manganese compound, a lithium compound, and the compound of a content other type element.

[0046] Furthermore, if it can be made homogeneity when mixing a raw material, it is also suitable to calcinate being able to adopt any methods of the usual method and mixing like rotary kiln.

[0047] As for the manufactured Spinel structure lithium manganese system oxide, it is desirable to perform grinding and a classification timely.

[0048] In this invention, Li rechargeable battery using the Spinel structure lithium manganese system oxide manufactured as mentioned above as positive active material was produced.

[0049] The material which can occlusion emit a lithium or a lithium ion can be used for the

negative-electrode active material used with the lithium secondary battery of this invention at a metal lithium list. For example, a metal lithium, a lithium / aluminium alloy, a lithium / tin alloy, a lithium/lead alloy, and the carbon system material electrochemically inserted and desorbed from a lithium ion are illustrated, and insertion and the carbon system material which de\*\* are electrochemically suitable especially from the field of safety and the property of a cell in a lithium ion.

[0050] Moreover, as an electrolyte used with the lithium secondary battery of this invention, although there is especially no limit, it can use what dissolved lithium salt, and the solid electrolyte of lithium ion conductivity into organic solvents, such as carbonate, sulfolanes, lactone, and ether, for example.

[0051] The Spinel structure lithium manganese system oxide of this invention was used for positive active material, and the cell shown in drawing 1 was constituted.

[0052] The lead wire for 1:positive electrodes, the mesh for 2:positive-electrode current collection, 3:positive electrode, 4:separator, 5:negative electrode, the mesh for 6:negative-electrode current collection, the lead wire for 7:negative electrodes, and 8:container are shown all over drawing.

[0053] In this invention, a stable highly efficient lithium secondary battery can be obtained using the positive active material, the negative-electrode active material, and lithium salt content nonaqueous electrolyte which have been described above.

[0054] Although an example is described below, this invention is not limited to this.

[0055]

[Example] Each measurement in the example and the example of a comparison of this invention was carried out on condition that the following.

[0056] - The XRD pattern was measured on condition that the following.

[0057]

Measurement model : Mac Saiensu-Sha MXP-3 exposure X-ray : Cu K alpha-rays  
measurement mode : Step scan scan conditions: Per second 0.04-degree measurement time amount : 3-second measuring range : 80 degrees and a component analysis were performed by ICP spectroscopy from 5 times as 2theta.

[0058] - Whenever [ oxidation / of Mn element ] was performed by the oxalic acid method.

[0059] As "composition of Spinel structure lithium manganese system oxide" example, and an example of a comparison, it compounded by the following methods.

[0060] Cr is used as an example 1 - a 5 other-type element M. MnO<sub>2</sub> (electrolytic manganese dioxide by TOSOH CORP.) whose diameter of average floc is 20 micrometers, the lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) whose BET specific surface area is 3m<sup>2</sup>/g, and the chrome oxide (Cr<sub>2</sub>O<sub>3</sub>) whose diameter of average floc is 1 micrometer change the ratio of Cr and Mn. After having carried out weighing capacity of the amount of Li(s) in the following empirical formulas so that the value of x might become fixed by 0.06 (Li:(Li+Mn+Cr) =1.06:3.00), often mixing with a mortar and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours.

[0061]

The photograph which observed the particulate structure of the Spinel structure lithium manganese system oxide obtained in the Li<sub>0.06</sub> and {Li} [Cry-Mn(2-0.06-y)] O<sub>4</sub> example 3 by one 20,000 times the scale factor of this using SEM is shown in drawing 2.

[0062] It became clear from this drawing that all the diameters of a particle primary particle of the Spinel structure lithium manganese system oxide obtained in the example 3 are 1 micrometer or less, and the first [ an average of ] particle diameter is 1 micrometer or less.

[0063] Moreover, it presumed that the structure of the obtained Spinel structure lithium manganese system oxide was the above-mentioned chemical formula by the lattice constant value and Rietveld analysis by the X diffraction.

[0064] In example 6 example 3, the last burning temperature was made the same from 750 degrees C except having made it high at 900 degrees C.

[0065] The photograph which observed the particulate structure of the obtained Spinel structure lithium manganese system oxide by one 20,000 times the scale factor of this using SEM is shown in drawing 3.

[0066] The diameter of a primary particle of the obtained Spinel structure lithium manganese system oxide became clear [ the thing of particle diameter / first / an average of / which is included also for a particle 1 micrometers or more and which is 3 micrometers or less ] from this drawing, although it was.

[0067] Except that the amount of Li(s) was made for the value of x to be set to 0.02 in example 7 example 4, it was presupposed that it is the same.

[0068] It was presupposed except having used Co instead of Cr in eight to example 10 examples 2-4 that it is the same.

[0069] In addition, Co raw material used basic cobalt carbonate.

[0070] It was presupposed except having used nickel instead of Cr in 11 to example 13 examples 2-4 that it is the same.

[0071] In addition, nickel raw material used basic nickel carbonate.

[0072] It was presupposed except having used Fe instead of Cr in 14 to example 16 examples 2-4 that it is the same.

[0073] In addition, Fe raw material used Fe 3O4.

[0074] As an other type element M1 of the example 17 first, carry out Fe use as second other type element M2, and Cr is set to the following empirical formula. The value of x the amount of Li(s) 0.01 (Li:(Li+Mn+Cr+Fe) =1.01:3.00), The value of y1 carries out weighing capacity of Cr 2O3 which are MnO2 whose diameter of floc is 20 micrometers so that the value of 0.1 and y2 may be set to 0.1, Li2CO3 whose BET specific surface area is 3m2/g, and 1 micrometer of diameters of average floc, and Fe3O4. After often mixing with a mortar and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours. After having carried out weighing capacity of MnO2 (electrolytic manganese dioxide by TOSOH CORP.) whose diameter of Li0.01, Cr0.1, Fe0.1, and example of {Li} [Mn1.79] O4 comparison 1 floc is 20 micrometers, and the lithium carbonate whose BET specific surface area is 3m2/g so that it might be set to x= 0.0 (Li:Mn=1.00:2.0), often mixing with a mortar and carrying out temporary quenching at 450 degrees C for 24 hours, it calcinated at 750 degrees C for 24 hours.

[0075] The product showed the same pattern as LiMn 2O4 of the JCPDS card 35-782.

[0076] It carried out on the same conditions as the example 1 of a comparison except having been referred to as x= 0.06 (Li:Li+Mn=1.06:3.0) in the example 1 of example of comparison 2 comparison.

[0077] It carried out on the same conditions as the example 1 of a comparison except having been referred to as x= 0.10 (Li:Li+Mn=1.10:3.0) in the example 1 of example of comparison 3 comparison.

[0078] It mixed so that it might be set to example of comparison 4 Li:Cr:Mn=0.95:0.2:1.80, and it calcinated on condition that the example 1 of a comparison.

[0079] The product of an example and the example of a comparison was cubic Spinel structure single phase except example of comparison 4.

[0080] It sank into 15ml of electrolytic solutions which dissolved [ the lithium manganese system oxide produced in "Mn elution test" example and the example of a comparison ] each the 6 phosphorus-fluoride acid lithium for 3g in the mixed solvent of ethylene carbonate and dimethyl carbonate by the concentration of one mol / dm3, and the 85 degrees C of the amounts of Mn after holding for 100 hours and in the electrolytic solution were analyzed by ICP spectroscopy.

[0081] The result was shown in a table 1.

[0082]

[A table 1]

	Li量 (x)	他種元素		Mn溶出量 (mol%)	格子定数 (Å)	BET (m <sup>2</sup> /g)	初期容量 (mAh/g)	容量維持率(%)		溶出試験維持率 (%)
		M	y					室温	50℃	
実施例1	0.06	Cr	0.01	0.65	8.237	1.75	120	--	--	--
実施例2	0.06	Cr	0.02	0.49	8.235	1.58	120	--	--	--
実施例3	0.06	Cr	0.1	0.09	8.230	2.31	108	99	94	90
実施例4	0.06	Cr	0.2	0.11	8.223	1.83	94	99	95	95
実施例5	0.06	Cr	0.4	0.14	8.209	1.80	63	97	95	95
実施例6	0.06	Cr	0.1	0.07	8.237	0.90	103	99	94	90
実施例7	0.02	Cr	0.2	0.20	8.242	2.11	115	95	90	85
実施例8	0.06	Co	0.02	0.64	8.231	1.41	120	--	--	--
実施例9	0.06	Co	0.1	0.52	8.228	1.60	108	96	91	81
実施例10	0.06	Co	0.2	0.49	8.196	1.43	93	96	92	85
実施例11	0.06	Ni	0.02	0.62	8.234	1.56	117	--	--	--
実施例12	0.06	Ni	0.1	0.23	8.219	1.73	93	95	92	88
実施例13	0.06	Ni	0.2	0.13	8.202	1.66	63	96	92	90
実施例14	0.06	Fe	0.02	0.49	8.235	1.68	120	90	88	81
実施例15	0.06	Fe	0.1	0.31	8.237	2.11	108	92	90	85
実施例16	0.06	Fe	0.2	0.18	8.234	2.12	93	99	95	96
実施例17	0.01	Cr Fe	0.1 0.1	0.05	8.239	1.88	107	99	95	94
比較例1	1.00	--	0.0	1.06	8.242	1.80	130	90	60	60
比較例2	1.06	--	0.0	0.84	8.234	1.75	123	94	83	75
比較例3	1.10	--	0.0	0.83	8.218	1.62	106	95	84	76
比較例4	0.95	Cr	0.2	0.95	---	1.70	---	--	--	--

[0083] The cell trial was performed using the sample after the lithium manganese system oxide obtained in the "configuration of cell" example, and the example of a comparison, and said Mn elution test. The cell trial mixed a sample, the polytetrafluoroethylene of an electric conduction agent, and the mixture (trade name: TAB-2) of acetylene black at a rate of 2:1 by the weight ratio. After fabricating mixture by the pressure of 1 ton/cm<sup>2</sup> on a mesh (SUS 316) at a pellet type, reduced pressure drying was carried out at 200 degrees C for 24 hours.

[0084] Thus, use the obtained pellet for the positive electrode of 3 of drawing 1, and the lithium piece clipped out from a lithium foil (0.2mm in thickness) is used for the negative electrode of 5 of drawing 1. The separator of 4 of drawing 1 is made to carry out impregnation of the solution which dissolved the 6 phosphorus-fluoride acid lithium in the mixed solvent of propylene carbonate and diethyl carbonate by the concentration of one mol / dm<sup>3</sup> to the electrolytic solution. Moreover, the cell which showed the lithium ion electrochemically to the negative electrode at drawing 1 using the carbon system material from which it is inserted and desorbed was constituted.

[0085] The lithium manganese system oxide produced in "evaluation of cell property" example and the example of a comparison was used for positive active material, the cell was produced, and cell voltage repeated charge and discharge between 4.5V and 3.5V with the fixed current of 1.0 mA/cm<sup>2</sup>.

[0086] The test temperature was carried out at a room temperature and 50 degrees C.

[0087] Initial capacity, the capacity maintenance factor (% of the discharge capacity of 50 cycle eye to 10 cycle eye), and the elution test maintenance factor (% to the initial capacity before the elution test of the capacity after an elution test) were shown in a table 1.

[0088]

[Effect of the Invention] There is little Mn elution in an organic solvent, and even if the Spinel

structure lithium manganese system oxide of this invention demonstrates the charge-and-discharge cycle nature stabilized by even after the mothball and performs charge and discharge at an elevated temperature further, there is little deterioration.

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[Translation done.]